FACILITY FORM 602

N65 16258	
(ACCESSION NUMBER)	(THRU)
18	1
(PAGES)	(CODE)
CR-60542	33
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

GPO PRICE $ ______

OTS PRICE(S) $ ______

Hard copy (HC) 1.00

Microfiche (MF) .50

RESEARCH ON LOW DENSITY
THERMAL INSULATION MATERIALS
FOR USE ABOVE 3000°F

Third Quarterly Status Report

Contract NASw-884

National Beryllia Corporation
Haskell, New Jersey

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Contract NASw-884
National Aeronautics and Space Administration

Third Quarterly Status Report
for the Period July 1 through September 30, 1964

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ABSTRACT

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Research on heat-transfer phenomena in low-density ceramic foam insulation is described, with emphasis on the properties of composite foams containing dispersed metallic additives. Physical properties of high-purity zirconia raw materials are discussed as they affect foam properties. Problems related to thermal stress effects in ceramic foams are described along with equipment calibration using ASTM standard specimens. Measured thermal conductivity data for tungsten-modified zirconia foams is presented in comparison with unloaded foam. Author

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(1) INTRODUCTION

This is the third quarterly report of Contract NASw-884 on the subject, "Research on Low Density Thermal Insulation Materials for Use above 3000°F". This program is a continuation of work performed on Contract NASr-99 which was conducted for seven quarters from April, 1962, through December, 1963.

1.1 Purpose of the Program

Low-density foamed ceramic thermal insulation rapidly loses efficiency above 2400°F due to the transfer of heat through the pores by thermal radiation. The purpose of this program is to study the reduction of this radiation or photon contribution to the thermal conductivity by the incorporation of a thermal radiation barrier phase into a low-density refractory structure. Mechanisms such as absorption and re-radiation by embedded particles, scattering by incorporated phases and reflection by metallic foil radiation barriers are being investigated and evaluated.

1.2 Phases of the Program

The goals of this program are being achieved through the pursuit of the three phases described briefly below with details of the progress made during this quarter discussed in Section II

Phase I - Technical Review

Review of previous high temperature heat transfer work, essentially completed during the first quarter, has been continued at a sufficient level of effort to keep abreast of the rapidly changing technology.

Phase II - Materials Formulation

The major effort of the program is concerned with the fabrication of low-density, low thermal conductivity materials. Light weight pure oxide ceramic matrices have been developed and impregnated with various volume percentages of potential radiation shielding phases introduced by a variety of techniques. Specimens of ceramic oxides whose thermal conductivity have been previously reported have also been prepared for calibration and equipment checkout purposes.

Phase III - Experimental Measurements

Evaluation of the thermal radiation barrier concept is being conducted in this phase of the program. A high temperature thermal conductivity test cell, capable of maintaining under steady conditions, specimen hot face temperatures of 4500^{o}F and above has been fabricated and calibrated. Measurement of the apparent total conductivity of the ceramic foam composite test samples is in progress.

(2) DISCUSSION

2.1 Technical Review

A report entitled, "A Radial Heat Flow Apparatus for High Temperature Thermal Conductivity Measurements", by A. D. Feith,[1] of the General Electric Company, dated August 31, 1964, was reviewed and found to support the data obtained on the NASA-National Beryllia Corporation equipment developed under the present programs. Comparative measurements of thermal conductivity of dense specimens of beryllium oxide and zirconium oxide were in close agreement with those obtained on similar specimens in the NASA-NBC apparatus. In his summary Mr. Feith concludes, "The major components of this effective or total thermal conductivity are the lattice (phonon) or true conductivity, electronic conductivity, radiative heat transfer and ambipolar diffusion. To make a comprehensive analysis of the data from the thermal conductivity test, the effect of temperature on each of these major components must be known. However, some of this vital information, (i.e. high temperature optical transport properties for radiative transfer determinations), is lacking and the final analysis of the behavior of the effective conductivity as a function of temperature for a given material is based on speculation and the probability that these other modes exist. Therefore, special studies should be made on each material of interest to determine these necessary properties, if a thorough quantitative analysis is desired."

Mr. Feith reports measurements of calcia stabilized zirconia specimens and similar specimens containing, however, 8 percent zirconium metal. His date indicates an attenuation of the radiative component of thermal conductivity in the zirconia specimen containing the metallic phase at temperatures up to 2000°C (3632°F). Subsequent communication with Mr. Feith has also shown close agreement on zirconia foam specimens between measurements on the G. E. thermal conductivity apparatus of similar radial heat flow concept but vastly differing experimental complexity and the NASA-NBC equipment.

The technical paper, "A Multiple Gauge Section Technique for the Measurement of Thermal Conductivity of Ceramic Foam Composites to 5000°F" was presented July 16, 1964, at the International Thermal Conductivity Conference, Teddington, England Resulting technical discussions resolved several questions concerning the source of scatter in the measurements and the most satisfactory averaging techniques from which reasonably smooth curves may be produced.

2.2.1 Matrix Formulations

A comparison of two lots of the high purity zirconium dioxide powders used in the preparation of the Zr36 foamed zirconia matrix has been completed. Results are tabulated in Table I. It is apparent that lot-to-lot variation is significantly less for this source, as indicated by physical property tests of fabricated samples, at least for these two lots which were acquired three months apart. Considerable improvement is noted over other sources previously used in which a lot-to-lot variation was extremely troublesome.

These experiments were conducted at fixed percentage compositions of foaming agents, organic setting agents and calcia stabilizing compounds. Batch sizes were, in all cases, identical and processing conditions of mixing equipment, speed and time held constant. The one variation reported, that of milling time in a small laboratory alumina ball mill, allows a variation in density and strength at the expense of minor alumina contamination. Milling in rubber-lined mills with zirconia media is considerably less effective but circumvents the contamination problem for extreme temperature applications.

2.2.2 Composites

Zirconia composite specimens, based on a Zr36 matrix, have been prepared containing tungsten metal and molybdenum disilicide additions. Structures were obtained which adequately

TABLE I

LOT TO LOT AND MILLING VARIATIONS

Property	(A) Powder as Received		(B) Powder Milled 2 Hrs.		(C) 50-50 Blend A and B		(D) Powder Milled 6 Hrs.		(E) Powder Milled 12 Hrs.	
	Lot 1	Lot 2	Lot 1	Lot 2	Lot 1	Lot 2	Lot 1	Lot 2	Lot 1	Lot 2
Part.Size Longest Dim. Optically (μ)	40-55	35-45	10-25	20-25	10-55	20-45	10-20	15-20	10-20	15-20
Fired Foam Properties										
1. Density (g/cc)	1.13	1.14	0.69	0.55	0.81	0.90	0.50	0.64	Poor Green Strength	
2. % Theoretical Density	20.2	20.4	10.7	9.0	14.5	16.1	8.9	11.4	- -	
3. Avg.Pore Size (μ)	328	390	390	637	320	407	354	334	- -	
4. Porosity (%)	79.8	79.6	89.3	91.0	85.5	83.9	91.9	88.6	- -	
5. Strength (MofR psi)	680	575	530	435	720	510	520	410	Weak	

simulate the density and average pore size of the unloaded foamed ceramic, with density increases due only to the phases added. These materials were fabricated into cylindrical thermal conductivity specimens and measured, as reported in section 2.3.2.

The extremely high temperature gradients, approaching 4000^{o}F per inch within the composite insulation, causes unusually high thermal stresses within the test sample. These high stresses result, in many cases, in mechanical failure in the form of radial cracks, usually in the region of the smallest cross sectional area, such as sight hole locations. For these reasons, ceramic foams of highest mechanical strength are required. It may be noted in Table I that foam Zr36, the P.P.G. powder wet milled for 6 hours, does not yield the highest strength product. Additional experimental work is therefore in progress to develop higher strength zirconia composites so that the high thermal stresses encountered may be withstood.

Several additional methods of incorporating radiation barrier phases were investigated during the report period. Tungsten metal was deposited within a fired zirconia foam by the thermal decomposition of a tungsten halide gas. This process yields a deposit somewhat more heavy in the areas nearest to the point where the halide is introduced. Tungsten metal, as confirmed by x-ray diffraction, is however, deposited continuously throughout the foam structure. This technique will be useful in positioning tungsten coatings primarily in regions where they will be the most efficient thermal radiation barriers, e.e., the potential hot face surfaces of the insulation system.

Another technique for the introduction of tungsten metal is by the decomposition of ammonium tungstate. This can readily be introduced into the porous foam by vacuum impregnation of a water suspension or solution. Subsequent drying and firing in hydrogen reduced it to metallic tungsten. Samples of zirconia foam impregnated by this method showed thorough penetration of all pores and a uniformly thin coating over all pore surfaces.

A similar test starting with a water suspension of tungstic acid showed uneven penetration and concentration of tungsten on the outer surface. This technique may also be applicable to applications wherein the tungsten coating is desired primarily in the hot face region.

2.3 Phase III Experimental Measurements

2.3.1 Verification of Test Data

In order for the experimental measurements accumulated and reported during the course of the program to be meaningful it is not only advisable but necessary to periodically measure specimens of known thermal conductivity. Appendixed to the previous quarterly report is a copy of the technical paper presented at the July, 1964, International Thermal Conductivity Conference, Teddington, England, which contains comparative data from the NASA-National Beryllia Corporation's radial heat flow apparatus and measurements on similarly processed dense zirconia specimens conducted at the Southern Research Institute. Aside from some scatter inherent in the multiple gauge section procedure, agreement was good in two runs in which a relatively new graphite hairpin heater was used.

A decrease in cross-sectional area of the heater with use and age, accompanied by an increase in resistance and lower current and wattage values at given applied voltages has been previously reported.[2] In order to determine the effect of this condition on measurement accuracy, a stack of BeO specimens, obtained from ASTM Committee C25 as part of a round robin measurement program, was measured in run No. 64 using a heater which had seen considerable service. Resulting data are plotted in Figure 1, which includes curves established by the American Lava Corp. and by Melpar, Inc., along with data points from the

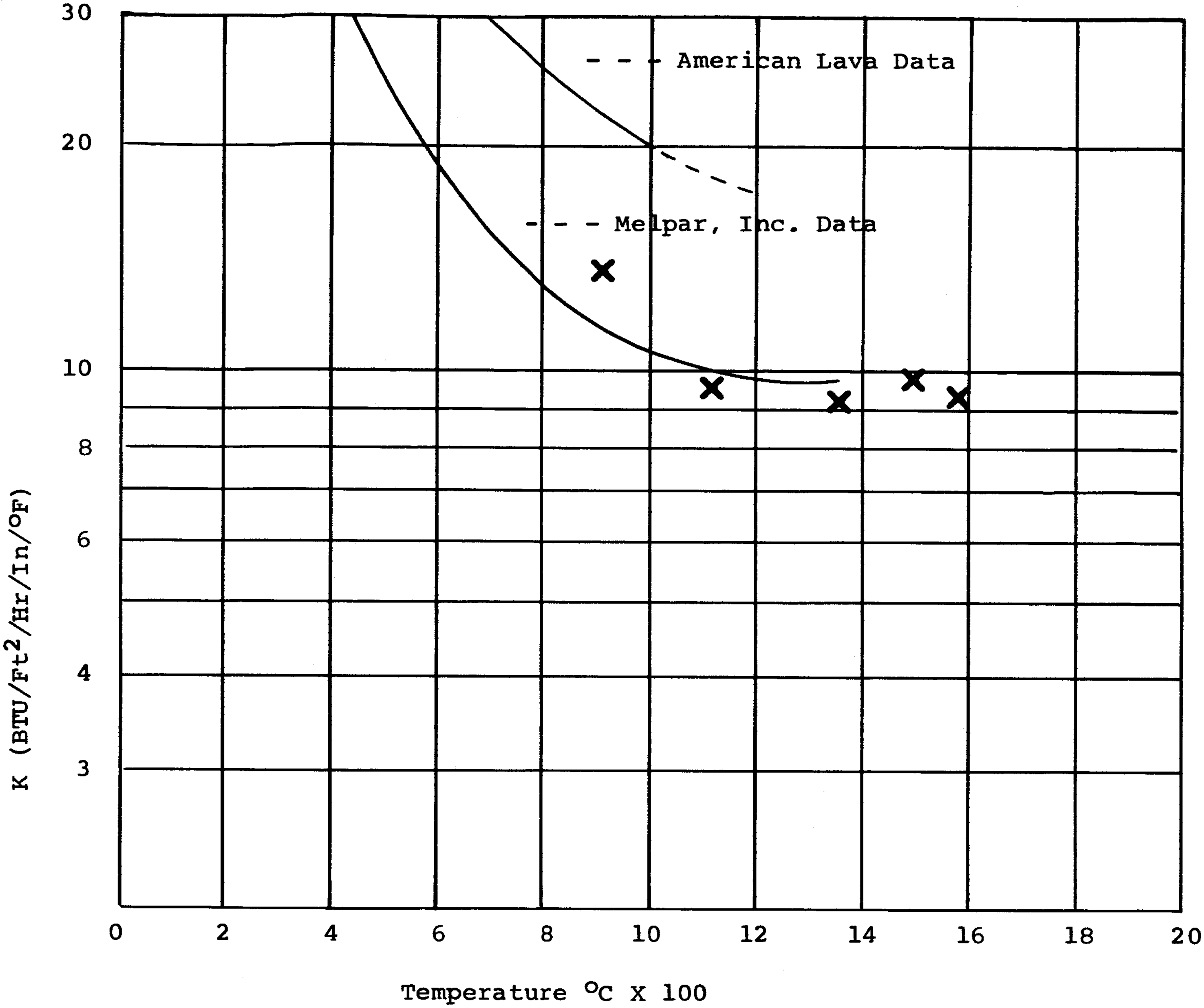


Figure 1

THERMAL CONDUCTIVITY -VS- TEMPERATURE
Results of Round Robin Test on Brush Beryllium Co,
Electronic Grade BeO

X - Data points from NASA/NBC radial
heat flow apparatus - Run No. 64

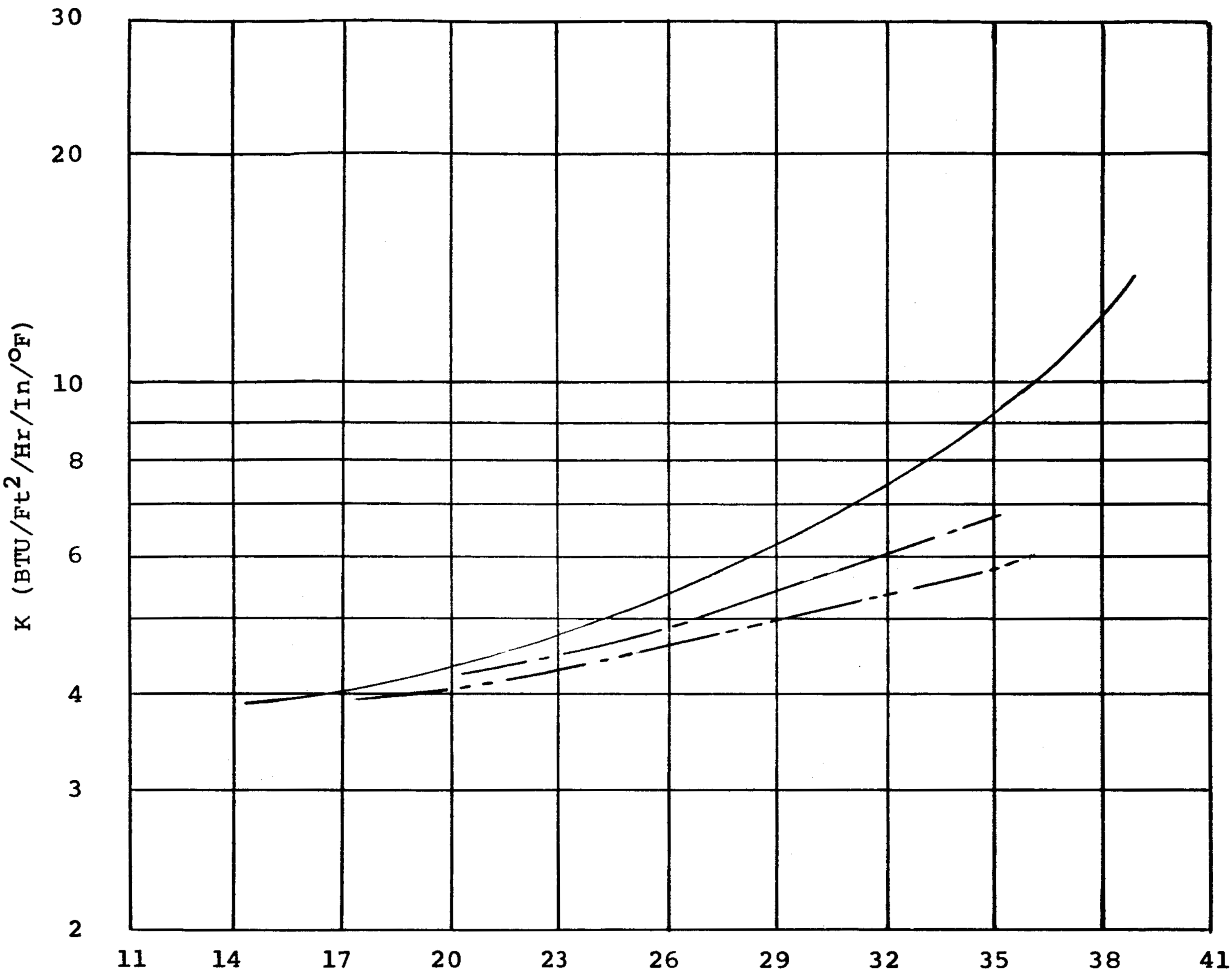
from the NASA-NBC apparatus. Agreement is excellent with the Melpar, Inc. results. Additional measurements are scheduled on Southern Research Institute equipment and to higher temperatures on the NASA-NBC apparatus using a new graphite heater.

2.3.2 Composite Measurements

Figure 2 is a plot of thermal conductivity versus temperature for Zr36 type zirconia foams, both plain with no added phases and with 20 percent by weight of tungsten metal and 20 percent molybdenum disilicide. The curve of plain Zr36 foam is a composite from three specimens and agrees well with many previous measurements of Zr28 type foams. The curves of the samples with the tungsten and molybdenum disilicide additions are the results of single specimens, both of which exhibited mechanical failure at high temperatures. High temperature results are therefore preliminary and must be varified when mechanically stronger composite foam specimens are developed.

(3) PROGRAM FOR NEXT QUARTER

Efforts will continue to develop foam structures of improved physical strength. Specimens will then be prepared, containing thermal radiation barrier phases, which will be better able to withstand the severe thermal stresses caused by the 4000°F thermal gradients which they can develop.



Temperature ^{o}F X 100

Figure 2

THERMAL CONDUCTIVITY -VS- TEMPERATURE

——————— Average Curve Zr36 ZrO_2 Foam

—— – —— Average Curve Zr36 ZrO_2 Foam with 20 w/o $MoSi_2$ addition

——-·-—— Average Curve Zr36 ZrO_2 Foam with 20 w/o W metal addition

Specimens of zirconia foam, containing zirconium metal powder will be prepared and measured in efforts to duplicate and substantiate the General Electric Co. data recently reported.

Thermal conductivity data on all samples prepared during this quarter will be obtained and correlated with previous data in preparation for the final report.

REFERENCES

1) Feith, A. D., "A radial Heat Flow Apparatus for High-Temperature Thermal Conductivity Measurement". General Electric Co., GEMP-296, August, 1964.

2) Styhr, K. H., "Research on Low Density Thermal Insulation Materials for Use Above 3000°F", First Quarterly Status Report, Contract NASw-884, National Beryllia Corp. April, 1964.